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# ELECTRON SPIN RESONANCE OF PHOTOCHROMIC $\beta$ -TETRACHLORO- $\alpha$ -KETONAPHTHALENE

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A triplet ESR spectrum has been observed in a powdered sample of  $\beta$  2,3,4,4-tetra-chloro- $\alpha$ -keto-naphthalene after UV irradiation. The spectrum could be reproduced by computer simulation using an anisotropic  $g$ -tensor ( $g_{xx} = 2.00950$ ,  $g_{yy} = 2.00280$ ,  $g_{zz} = 2.00232$ ) and zero-field splitting parameters  $D$  and  $E$  of 99 and 2.3 gauss respectively. The results are discussed in terms of the earlier proposed photodissociation into a naphthoxyl radical and a chlorine atom.

In 1888 Zincke [1] observed that colourless crystals of  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene ( $\beta$ TKN) become amethyst coloured under the influence of light. Marckwald [2] recognized that this reaction is reversible and introduced the term "phototropy". Nowadays the phenomenon is generally called "photochromy". The first quantitative optical measurements were performed by Weigert [3] who found that the electronic transition moment of the absorption band that appeared upon radiation lies in the plane of the naphthalene ring.

Feichtmayr and Scheibe [4] have explained the photochromic behaviour of  $\beta$ TKN as a reversible photochemical dissociation reaction of the compound in the 2,3,4, trichloronaphthoxyl radical and a chlorine atom as is depicted in fig. 1. On the basis of Weigerts measurements they assign the new absorption band to a  $\pi$ - $\pi^*$  transition of the naphthoxyl radical.

Since the aromatic radical and the chlorine atom each carry a free electron spin, the crystal is expected to be paramagnetic in the "excited" state. An increase in the magnetic susceptibility upon radiation has indeed been found by Dörr and Engelman [5] but in spite of a number of attempts [6] no ESR spectrum has been re-

ported. We have started to reinvestigate the physics of the photochromic behaviour of  $\beta$ TKN and we report here the first results of our ESR measurements. After irradiating a powder of  $\beta$ TKN at 77°K for 20 minutes with a superhigh pressure mercury arc type HP 125 W, an ESR spectrum is obtained as shown in fig. 2. As is immediately clear from the lineshape of this spectrum and from the fact that at 'half field' a weak ESR signal can be detected ( $\Delta m = 2$  transition) this spectrum arises from the magnetic coupling between two unpaired electron spins. To make this interpretation more reliable we have made a computer simulation [7] of the spectrum based on the spin Hamiltonian

$$\mathcal{H} = \beta H \cdot g \cdot S + DS_z^2 + E(S_x^2 - S_y^2) \quad (1)$$

where  $g$  is the anisotropic  $g$ -tensor,  $D$  and  $E$  are the zero-field splitting (z.f.s.) parameters and  $S = S_1 + S_2$ .

The result of such a simulation is also shown in fig. 2, where a reasonable fit to the experimental spectrum could be obtained with the constants inserted in the figure. The parameter  $E$  turned out to be essential to reproduce the details of the spectrum in spite of its smallness ( $E/D = 0.02$ ). As can be seen from fig. 2 the experimental ESR spectrum shows a marked asymmetry. This can be understood as follows: from a first order analysis based on the Hamiltonian (1) stationarity in the resonance fields is obtained for the magnetic field along the principal axes of the z.f.s. tensor [8]. For a random orientation of the "triplet-molecules" some structure is thus produced in the

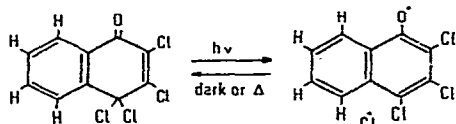


Fig. 1. The photodissociation of  $\beta$ TKN.

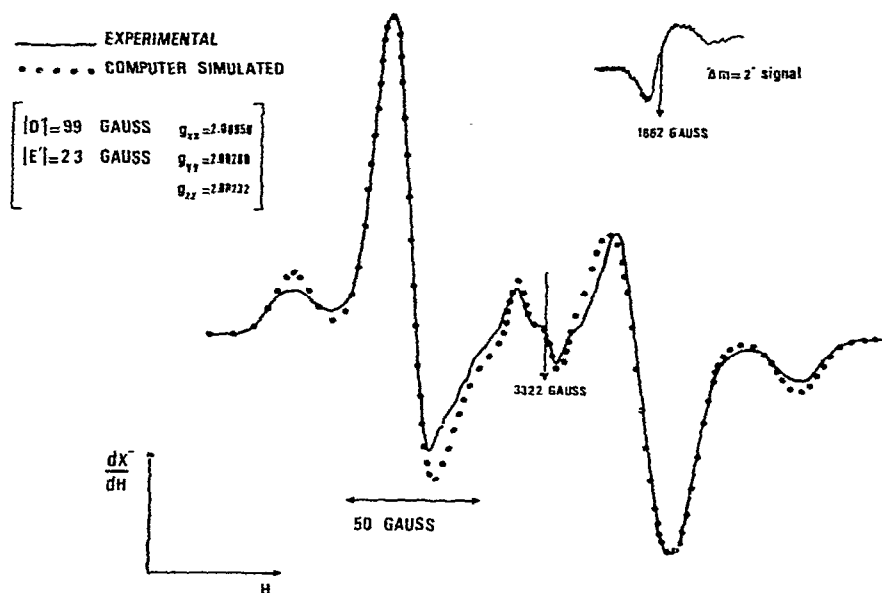


Fig. 2. Experimental and computer simulated ESR spectrum of UV irradiated BTKN powder.

absorption at these magnetic field values. These fields are called the axial resonance fields and it can easily be shown that in a first order approximation these axial fields occur at

$$\frac{g_e}{g_{xx}} [H_0 \pm \frac{1}{2}(D' - 3E')],$$

$$\frac{g_e}{g_{yy}} [H_0 \pm \frac{1}{2}(D' + 3E')],$$

and

$$\frac{g_e}{g_{zz}} (H_0 \mp D')$$

where  $D' = D/g_e\beta$ ,  $E' = E/g_e\beta$  and  $H_0 = h\nu/g_e\beta$ . Without  $g$ -anisotropy, the triplet ESR spectrum becomes symmetric (fig. 3a), but with  $g$ -anisotropy the spectrum becomes asymmetric (fig. 3b). In the case at hand a narrowing at low field and a broadening at high field of the spectrum occurs. Before discussing the z.f.s. constants we shall consider the central weak absorptions, which do not belong to the spectrum just discussed. These absorptions can be included in the simulation assuming a second two-electron spin system with very small z.f.s. parameters ( $D' = 12$  gauss,  $E' = 0$ ,  $g_{xx} = g_{yy} = 2.00400$ ,  $g_{zz} = g_e = 2.00232$ ). We can interpret our observations in terms of the dissociation mechanism proposed by Feichtmayr and Scheibe [4] together with one consecutive reaction. We consider the triplet spectrum as arising

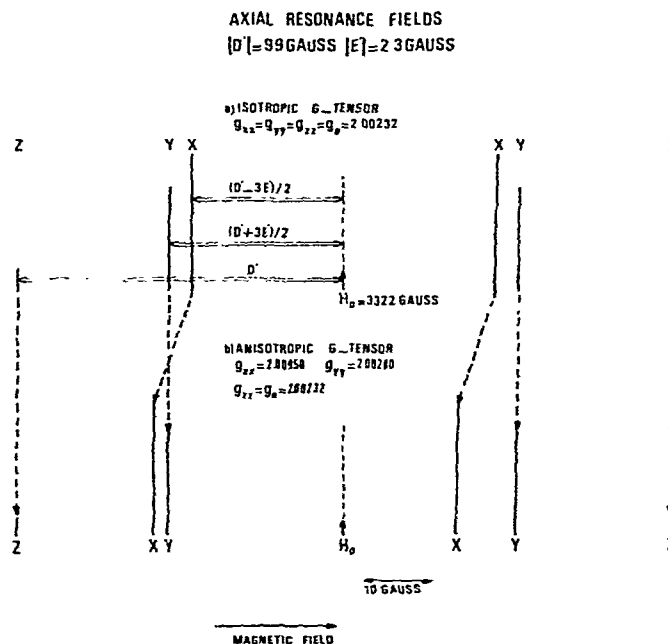


Fig. 3. The position of the axial resonance fields for an isotropic and anisotropic  $g$ -tensor. At X, Y and Z the magnetic field lies along the x, y and z-axis of the z.f.s. tensor.

ing from the magnetic coupling between a naphthoxyl radical and a chlorine atom while the central weak lines are probably due to the interaction between two naphthoxyl radicals.

In the latter case the chlorine atom initially formed abstracts a similar chlorine atom from a neighbouring ring. This reaction is similar to that observed by Kurita [9] after gamma-irradiation of oximes where initially formed hydrogen atoms react with hydrogen atoms from neighbouring oximes to form molecular hydrogen.

From the formula  $D = \frac{2}{3}g\beta\hbar r^{-3}$ , one finds the value of 6.5 Å for the effective distance between the two unpaired spins. Let us assume in a first approximation that the triplet electrons are localized on the oxygen of the naphthoxyl radical and the free chlorine atom respectively. In this approximation the OCl-distance in the excited state is thus 6.5 Å. In fact delocalization of the electron on oxygen will occur so that the actual OCl-distance in the excited state can be somewhat smaller to yield the same  $D$ -value. A comparison with the OCl-distance of 5.4 Å [10] in the parent compound thus leads us to conclude that the chlorine atom moves only over a very small distance after leaving the ring, and it is therefore not surprising that a recombination reaction occurs. So far we have not discussed the fact that near the triplet state also a singlet state must be expected. The gap between these two states can be derived from temperature dependent measurements of the magnetic susceptibility assuming a temperature dependence

$$\chi = C[T(3 + e^{J/kT})]^{-1},$$

where  $C$  is a constant and  $J$  the magnitude of the gap. Tentative measurements yield for  $J$  a value of  $\approx 20 \text{ cm}^{-1}$ , with the singlet state as the ground state.

The lowering of the singlet state with respect to the triplet state may well be due to a mixing of the zero order singlet state  ${}^1\phi_1(R_{\pi}^{\cdot}, \text{Cl}^{\cdot})$  with

the charge transfer state  ${}^1\phi_{\text{CT}}(R_{\pi}^{\cdot}, \text{Cl}^{\cdot})$ . This charge transfer excitation incidentally offers an alternative explanation for the intense absorption in the visible by the newly formed radical system which has hitherto been assigned to a  $\pi - \pi^*$  transition of the naphthoxyl radical. Optical and ESR measurements on single crystals are now in progress to clarify this and other questions pertaining to a better physical understanding of the photochromic behaviour of the compound at hand.

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#### REFERENCES

- [1] F. Zincke and O. Kegel. Ber. 21 (1888) 1027.
- [2] W. Marckwald. Z. Physik. Chem. 30 (1899) 140.
- [3] F. Weigert. Z. f. Elektrochem. 24 (1918) 223.
- [4] F. Feichtmayr and G. Scheibe. Z. Naturforsch. 13B (1958) 51.
- [5] F. Dörr and F. Engelmann. Naturwissensch. 39 (1952) 397.
- [6] H. S. Gutowsky. R. L. Rutledge and J. H. Hunsberger. J. Chem. Phys. 29 (1958) 1183; F. Feichtmayr and G. Scheibe. Z. Naturforsch. 13B (1958) 51; G. Scheibe. Chem. Ing. Technik 31 (1959) 321; A. von Dobrogoiski. Thesis. T. H. München. 1954.
- [7] D. A. Wiersma and J. Kommandeur. Mol. Phys. 13 (1967) 241.
- [8] E. Wasserman. L. C. Snijder and W. A. Yager. J. Chem. Phys. 41 (1964) 1763.
- [9] Y. Kurita. J. Chem. Phys. 41 (1964) 3926.
- [10] W. Hoppe and R. Rauch. Z. Kristallogr. 115 (1960) 141.